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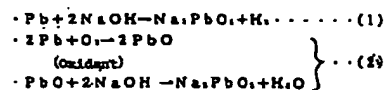
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179 Queen Victoria Street
London EC4V 4EL (GB)(54) **METHOD OF REDUCING ELUTION OF LEAD IN LEAD-CONTAINING COPPER ALLOY, AND CITY WATER SERVICE FITTINGS MADE OF LEAD-CONTAINING COPPER ALLOY**

(57) It is an object of the present invention to provide a processing method for preventing elution of lead in a lead-containing copper alloy to prevent lead from eluting from a faucet metal, etc. made of a lead-containing copper alloy, and a drinking water service fitting made of a lead-containing copper alloy in which elution of lead has been prevented. By forming a chromate film on the surface of a lead-containing copper alloy material, it is possible to reduce elution of the lead left in a limited amount on the surface. A drinking water service fitting made of a lead-containing copper alloy is immersed in an alkaline etching solution in a pre-processing step for a nickel chromium plating step to selectively remove lead on the surface of the lead-containing copper alloy material and is then activated in a solution such as sulfuric acid and hydrochloric acid. Nickel plating is subsequently effected, and then chromium plating is effected in a sargent chromium or chromium fluoride bath, and a chromate film may be formed by immersing the drinking water service fitting in a chromate solution.

FIG. 4.



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Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to a processing method for reducing elution of lead from a lead-containing copper alloy, a plating method for reducing elution of lead in a lead-containing copper alloy, and a drinking water service fitting made of a lead-containing copper alloy which exhibits reduced elution of lead.

[0002] The drinking water service fittings include those which are directly connected to a feed water pipe, such as water heater, water cooler, ice-maker, water purifier, hot water boiler, vending machine, pole tap, low tank, valve (faucet metals), joint, pipe, sink, wash stand, stool, bath tub, housing unit, etc.

2. Description of the Prior Art

[0003] Hitherto, faucet metals have been generally manufactured by casting or forging a copper alloy such as bronze or brass, cutting and polishing to shape, and then nickel chromium plating, etc.

[0004] To improve machinability of the copper alloy during cutting in a manufacturing process, lead is added to the copper alloy.

[0005] Figure 7 is a schematic view of composition of the copper alloy to which lead is added. When lead is added to the copper alloy 1, lead, lead oxide, lead hydroxide or the like gather near the surface of the copper alloy, while lead 2 exists as a simple substance in the inside thereof. The concentration of the lead 2 near the surface is several times higher than that of lead on the inside.

[0006] In the faucet metals made of bronze casting to which lead is added, lead of about 500ppb elutes. Thus, lead elutes from the surface of a water flow channel of the drinking water service fittings made of a lead-containing copper alloy into water and as a result, there is the possibility that drinking of such water for a long time will exert a bad influence on a human body.

[0007] However, copper alloy materials to which lead is not added has poor machinability, and a substitute copper alloy material has not yet been developed.

SUMMARY OF THE INVENTION

[0008] It is, therefore, an object of the present invention to provide a processing method for preventing elution of lead in a lead-containing copper alloy by removing lead from the surface of a lead-containing copper alloy material to prevent lead from eluting from a faucet metal, etc. made of a lead-containing copper alloy, a plating method for reducing elution of lead in a lead-containing copper alloy, and a drinking water service fitting made of a lead-containing copper alloy in

which elution of lead has been prevented.

[0009] The present invention pays attention to a property of lead as an amphoteric metal, wherein a lead-containing copper alloy is immersed in an alkaline etching solution to which an oxidant is added, to selectively dissolve and remove lead on the surface of a lead-containing copper alloy material.

[0010] Thus, both a chemical reaction whereby lead on the surface of a lead-containing copper alloy material contacts an alkaline solution so as to directly become an alkali metal salt of a water-soluble zincate, and a chemical reaction whereby the lead is first converted to lead oxide by an oxidant and this lead oxide is converted to an alkali metal salt of a water-soluble zincate by an alkaline solution, proceed together. However, the chemical reaction of the latter advances faster than that of the former and as a result, dissolution of lead is expedited to remove lead.

[0011] When this chemical reaction occurs, copper (a simple substance), tin forming an alloy together with copper, zinc, aluminum, etc. do not react to the alkaline solution, and only the lead (a simple substance) which does not form an alloy together with copper is selectively removed by the above-mentioned chemical reaction.

[0012] It is desirable to further add a chelating agent to this etching solution. By adding the chelating agent, lead is formed with a water-soluble complex and it is possible to effectively remove lead.

[0013] Further, it is desirable to form a chromate film on the surface of a lead-containing copper alloy material after lead on the surface of the lead-containing copper alloy material is dissolved and removed.

[0014] Namely, a chemical reaction that dissolves a lead-containing copper alloy, and a chemical reaction that forms a chromate film are caused by chromic acid contained in a chromate solution so as to dissolve and remove the lead left in a limited amount on the surface of a lead-containing copper alloy material. Also, the surface of the lead-containing copper alloy material from which lead has been removed is protected by a chromate film. Lead on the inside does not elute even though the surface of the lead-containing copper alloy material from which lead has been removed corrodes due to long term water flow. It is therefore possible to reduce elution of lead for a long period.

[0015] Further, the present invention pays attention to the point that in a plating step such as nickel chromium plating to be effected on a lead-containing copper alloy, this alloy is usually immersed in a plating solution. The outer surface of the lead-containing copper alloy is therefore plated and, at the same time, lead on the inner surface is dissolved and removed.

[0016] An alkaline degreasing solution is used as a pre-cleaning step for plating, but an oxidant is contained in the solution to expedite dissolution and removal of lead on the inner surface of a lead-containing copper alloy material. Also, addition of fluoride to a chromium

plating solution serves to effectively dissolve deposits of lead chromate.

[0017] Further, a lead-containing copper alloy material may be immersed in a chromate solution to form a chromate film on the inner surface thereof after plating the outer surface thereof. With this film formation, it is possible to reduce elution of lead left in a limited amount on the surface of the lead-containing copper alloy material. It is desirable to add a phosphoric acid to the chromate solution.

[0018] The lead-containing copper alloy material is degreased in an alkaline degreasing solution as a cleaning step before plating in a solution in which an oxidant is contained. Acid activation and nickel plating are subsequently effected and then, chromium plating is effected in a chromium plating solution that contains fluoride. Thus, it is possible to dissolve and remove lead on the inner surface of the lead-containing copper alloy material while effecting nickel chromium plating on the outer surface thereof.

[0019] Further, the lead-containing copper alloy material is degreased in an alkaline degreasing solution as a cleaning step before plating in a solution which contains an oxidant. Acid activation and nickel plating are subsequently effected and then, chromium plating is effected in a sargent chromium plating bath or a chromium fluoride plating bath. The lead-containing copper alloy material is further immersed in a chromate solution to form a chromate film on the inner surface thereof. It is possible to dissolve and remove lead on the inner surface of the lead-containing copper alloy material while effecting nickel chromium plating on the outer surface thereof. It is desirable to include a phosphoric acid in the chromate solution.

[0020] The faucet metals mainly use a lead-containing copper alloy material such as bronze or brass, and various plating steps are effected to improve the beauty of the outer surface, corrosion resistance, and wear and abrasion resistance. According to the present invention, plating is effected on the outer surface of the lead-containing copper alloy material while reducing elution of lead on the inner surface thereof at the same time. It is therefore possible to reduce elution of lead in various plating steps including nickel chromium plating.

BRIEF DESCRIPTION OF THE DRAWINGS

[0021]

Figure 1 is a view showing an elution effect on lead when lead elutes by alkaline etching;

Figure 2 is a view showing an analytical result of the concentration of lead elution when chromium plating bath treatment is effected after alkaline etching;

Figure 3 is a view showing an analytical result of the concentration of lead elution when a chromate process is effected after alkaline etching;

Figure 4 is a schematic view showing the condition

where lead has been eluted by alkaline etching:

Figure 5 is a schematic view showing the condition of a plating bath treatment in a chromium fluoride bath;

Figure 6 is a schematic view showing the condition of a chromate treatment; and

Figure 7 is a schematic view showing the composition of a copper alloy to which lead has been added.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0022] The present invention pays attention to the property of lead as an amphoteric metal, wherein a lead-containing copper alloy is immersed in an alkaline etching solution to which an oxidant has been added to selectively dissolve and remove lead on the surface of a lead-containing copper alloy material. Also, the lead-containing copper alloy is immersed in a chromic acid solution to dissolve lead on the surface thereof. It is also possible to dissolve and remove lead on the surface of the lead-containing copper alloy material by immersing the lead-containing copper alloy in the alkaline etching solution, and then immersing the same in a chromic acid solution. When any one or a plurality of an oxidant, chelating agent and surface active agent are added to the alkaline etching solution, and when fluoride is added to a chromic acid solution, it is possible to effectively remove lead.

[0023] A chromate film may also be formed on the surface of a lead-containing copper alloy material. With this film formation, it is possible to reduce elution of the lead left in a limited amount on the surface. A drinking water service fitting roads of a lead-containing copper alloy is immersed in an alkaline etching solution in a pre-processing step for a nickel chromium plating step to selectively remove lead on the surface of the lead-containing copper alloy material and is then activated in a solution such as sulfuric acid and hydrochloric acid. Nickel plating is subsequently effected, and then chromium plating is effected in a sargent chromium or chromium fluoride bath, and a chromate film may be formed by immersing the drinking water service fitting in a chromate solution.

[0024] When chromium plating is effected in a chromium fluoride plating bath where fluoride has been substituted for a part or all of sulfuric acid in a sargent bath consisting of ordinary sargent chromium or chromic acid anhydride and sulfuric acid, a chromic acid solution will not only dissolve the entire copper alloy material, but also dissolve lead because the chromic acid solution contained in a chrome plating bath is a strong acid.

[0025] Thus, it is possible to effect nickel chromium plating on the outer surface of the drinking water service fitting and at the same time, to remove lead on the surface of a water flow channel of the inner surface thereof.

[0026] A plating process usually consists of a degreasing step and a plating step. The degreasing

step is a step for removing stains such as a grease component attached to a material to secure adhesion of plating. A main component of the alkaline etching solution which is used in the present invention is an alkaline solution that has dissolved any one or several kinds of sodium hydroxide, potassium hydroxide, sodium carbonate, sodium phosphate, sodium tripolyphosphate, sodium metasilicate, sodium orthosilic acid, etc. The concentration is general between several grams/l and several tens of grams/l and it can be selectively decided depending on the combination of the components used therein.

[0027] A temperature of about 60° - 90° C is desirable because the higher the temperature, the higher the effect of lead elution. Immersion time of between several minutes and several tens of minutes is desirable. As shown in Figure 4, a copper metal does not generally infiltrate, but it is possible to selectively dissolve lead as an amphoteric metal. The plating process usually consists of a degreasing step and a plating step. The degreasing step is a step for removing stains such as a grease component attached to a material to secure the adhesion of plating. An alkaline etching solution used in the present invention acts as an alkaline degreasing solution.

[0028] To improve penetration and wettability of an alkaline etching solution, a surface-active agent is added for the purpose of reducing surface tension of the solution. An anionic surface-active agent or a nonionic surface-active agent is mainly used as the surface-active agent and these can be used alone or together. The anionic surface-active agent includes higher fatty acid sodium, sulfonated oil, higher alcohol sodium sulphate, alkylbenzene sodium sodium sulphate, higher alkyl ether sodium sulphate, and alpha olefin sodium sulphate.

[0029] Also, the nonionic surface-active agent includes alkyl polyoxyethylene ether, alkyl phenyl polyoxyethylene ether, fatty acid ethylene oxide adduct, polypropylene glycol ethylene oxide adduct (Pluronic). An amount of addition between several grams/l and several tens of grams/l is general.

[0030] It is also possible to add a chelating agent to prevent reattaching of lead as hydroxide and to expedite dissolution of lead. Desirable as the chelating agent, for example, is a chemical compound which can easily form a complex together with lead of EDTA, ethylene diamine, triethanolamine, thiourea, Rochelle salt and tartaric acid, etc. A concentration between several grams/l and several tens of grams/l is desirable for each component.

[0031] When an oxidant is added in an alkaline etching solution, lead is oxidized and dissolves in alkali through lead oxide (PbO, etc. [reaction formula (2) of Figure 4]. This reaction (2) is effected faster than the reaction (1) and as a result, expedites dissolving lead. Used as the oxidant, for example, are an organic oxidizing compound such as meta-nitrobenzene sodium sul-

fonate, P-nitro sodium benzoate, and an inorganic compound such as hypochlorite, bleaching powder, hydrogen peroxide, potassium permanganate, persulfate, and perchlorate. A concentration between several grams/l and several tens of grams/l is desirable for each component.

[0032] A chromium fluoride bath is available as a bath used for chromic acid immersion. This chromic fluoride bath can use a generally well-known sargent chromium plating bath, but the fluoride is substituted for a part or all of sulfuric acid in a sargent bath consisting of chromic acid anhydride and sulfuric acid.

[0033] When chromium plating is effected in a chromium plating solution, chromium plating is effected on the outer surface of a copper alloy material, but the entire part of the inner surface dissolves while lead dissolves because the chromium plating solution has strong acidic properties. However, there is the possibility that deposits remain as lead chromate when fluoride does not exist [reaction formula (3) in Figure 5]. Since fluoride serves to dissolve such deposits, it is desirable to effect chromium plating in the chromium fluoride bath [reaction formula (4) in Figure 5]. A temperature between 40°C and 60°C and immersion time between several tens of seconds and several minutes are desirable respectively.

[0034] Used as fluoride are almost all the fluorine compounds such as sodium fluoride, potassium, ammonium fluoride, hydrofluoric acid, boro-hydrofluoric acid, hydrofluosilic acid, sodium silicofluoride, potassium silicofluoride, and boro-chromium fluoride.

[0035] An additive agent used in a chromate processing is based on chromic acid anhydride, phosphoric acid and sulfuric acid, but nitric acid, hydrofluoric acid, acetic acid, oxalic acid, chromate, etc. are added or substituted as the case may be. A chromate agent such as a galvanizing agent on the market may be used.

[0036] A concentration between several grams/l and several tens of grams/l is desirable for each component. A processing temperature between room temperature and 60°C. and a processing time between several seconds and several minutes are desirable respectively. By immersing a completed product with its outer surface plated in this chromate solution, a chromate film can be formed on the inner surface by a reaction formula, as shown in Figure 6, to control elution of lead. By adding phosphoric acid to chromic acid anhydride which is the main component of the chromate solution, it is possible to improve the control effect of lead elution with a synergistic effect.

(1) Alkaline etching solution

[0037] A lead elution effect of the alkaline etching solution and a lead elution effect when an oxidant and a chelating agent are added to the alkaline etching solution are shown in Figure 1.

[0038] Processing is effected in the following steps.

Faucet metals made of bronze casting are immersed in various etching solutions as shown in Figure 1 for 3 minutes at 80°C, and then washed for 30 seconds. They are subsequently immersed in a chromium fluoride plating solution on the market with a fluorine contents of about 1 gram/l, for 3 minutes at 45°C and then washed for 30 seconds. These metals are subsequently washed with hot water for 30 seconds at 60°C.

[0039] Processed faucet metals were then analyzed to see the concentration of lead eluted in accordance with "Drinking water service fittings - Percolation performance test method" by JIS S 3200 - 7 (1977). Figure 4 is a schematic view showing the condition where lead is eluted by the alkaline etching, wherein lead 2 on the surface of a lead-containing copper alloy 1 is selectively removed by a reaction formula as shown in Figure 4.

[0040] As can be seen from the results in Figure 2, an untreated sample without etching has a lead elution amount of 500ppb, while the lead elution amount for the products treated according to the present invention is remarkably reduced. In particular, the lead elution amount of the treated products was further reduced by addition of the oxidant and the chelating agent. It is to be noted that immersion of the products in the chromium fluoride plating solution enables the lead elution amount to be reduced further.

(2) Chromium plating solution

[0041] Next, faucet metals made of bronze casting are immersed in an alkaline etching solution (sodium hydroxide 50g/l, meta-nitrobenzene sodium sulfonate 2g/l, EDTA 2g/l, ethylene diamine 2g/l) for 3 minutes at 80°C and then washed for 30 seconds. The faucet metals are subsequently immersed in a chromium plating solution as shown in Figure 2 for 3 minutes at 45°C, washed for 30 seconds, and then washed with hot water for 30 seconds at 60°C. The faucet metals were then analyzed to obtain the concentration of lead elution in accordance with JIB S 3200 - 7 (1997). The result of this analysis is shown in Figure 2.

[0042] As seen from Figure 2, the lead elution amount is remarkably reduced when immersed in the chromium plating solution, but the chromium fluoride bath is more effective than the conventional sargent chromium bath. The sargent bath where fluoride does not exist is considered to have had a slightly higher concentration of lead because deposits remain as lead chromate [reaction formula (3) of Figure 5]. The fluoride, which dissolves the deposits, is considered to have had a better effect in the chromium fluoride bath than the sargent chromium bath [reaction formula (4) of Figure 5]. It is also obvious that even immersion in chromic acid only has a lead elution effect.

(3) Chromate processing

[0043] Faucet metals made of bronze casting are immersed in an alkaline etching solution (sodium hydroxide 50g/l, meta-nitrobenzene sodium sulfonate 2g/l, EDTA 2g/l, ethylene diamine 2g/l) for 3 minutes at 80°C and then washed for 30 seconds. The faucet metals are subsequently immersed in a chromium fluoride plating solution (the above-mentioned bath on the market with a fluorine content of about 1g/l) for 3 minutes at 45°C and then, washed for 30 seconds. Next, chromate treatment is effected in a chromate solution with a composition as shown in Figure 3 for 20 seconds at 30°C, washed for 30 seconds, and washed with hot water for 30 seconds at 60°C.

[0044] The faucet metals are then analyzed to obtain the elution concentration of lead in accordance with JIS S 3200 - 7(1997). The analytic results are shown in Figure 3.

[0045] As shown in Figure 3, as compared with the case without chromate treatment, the lead elution amount of the product effected with chromate treatment is reduced, and the lead elution can be remarkably controlled, especially with the synergistic effect of chromic acid anhydride with phosphoric acid. Namely, with the synergistic effect of chromic acid and phosphoric acid contained in the chromate solution, a chemical reaction for dissolving a lead-containing copper alloy and a chemical reaction for forming chromate film are caused to remove the lead left in a limited amount on the surface of a lead-containing copper alloy material. By removing the lead, the chromate film is provided to protect the surface of the lead-containing copper alloy material. It is therefore possible to reduce elution of lead for a long time because the lead situated inside the lead-containing copper alloy material is not eluted even when the surface thereof corrodes due to water flow for a long time. With this chromate treatment, the chromate film is formed by a reaction formula in the schematic view showing the condition of chromate treatment in Figure 6 to control elution of lead. It is obvious that even the chromate treatment only has a good effect on the elution of lead.

[0046] According to the present invention, by immersing drinking water service fittings made of lead-containing copper alloy in an alkaline etching solution to which an oxidant is added to remove lead on the surface thereof, it is possible to effectively reduce elution of lead used in the drinking water service fittings. If a chelating agent is added to this etching solution, it is possible to further improve prevention of lead elution.

[0047] The drinking water service fittings made of a lead-containing copper alloy are immersed in an alkaline solution to which an oxidant is added to remove lead on the surface thereof. They are subsequently immersed in a chromate solution to form a chromate film on the surface thereof. With this film formation, it is possible to remarkably reduce elution of lead.

[0048] By immersing the drinking water service fittings made of a lead-containing copper alloy in a chromic acid solution to which fluoride has been added to remove lead on the surface thereof, it is possible to effectively reduce elution of lead used in the drinking water service fittings. 5

[0049] After the drinking water service fittings made of a lead-containing copper alloy are immersed in an alkaline etching solution to remove lead on the surface thereof, they are further immersed in a chromic acid solution to which fluoride has been added. With this immersion, it is possible to remarkably reduce elution of lead. 10

[0050] If an oxidant and a chelating agent are added to the etching solution, it is possible to further improve prevention of lead elution. 15

[0051] Since the drinking water service fittings made of a lead-containing copper alloy are immersed in a chromate solution to which phosphoric acid is added to form a chromate film thereon, it is possible to effectively reduce elution of lead used in the drinking water service fittings. 20

[0052] The drinking water service fittings made of a lead-containing copper alloy are immersed in an alkaline etching solution and then immersed in a chromic acid solution to remove lead on the surface thereof. Since they are subsequently immersed in a chromate solution to which phosphoric acid has been added to form a chromate film on the surface, it is possible to remarkably reduce elution of lead. 25

[0053] The drinking water service fittings made of a lead-containing copper alloy are immersed in a chromic acid solution to which fluoride has been added to remove lead on the surface thereof. Since they are subsequently immersed in a chromate solution to form a chromate film on the surface thereof, it is possible to reduce elution of lead from the inside thereof and to remarkably reduce elution of lead. 30

[0054] Further, when the alkaline etching solution is used as a pre-processing agent for plating, it is possible to improve degreasing strength of stains and oil on the surface of a material and at the same time, to improve the outer appearance and adhesion of plating. 35

[0055] Still further, the drinking water service fittings made of a lead-containing copper alloy are immersed in an alkaline solution to remove lead on the surface thereof, and then immersed in a chromic acid solution to further remove lead on the surface thereof. Since they are subsequently immersed in a chromate solution to form a chromate film, it is possible to remarkably reduce elution of lead. 40

Claims

1. (Amended) A processing method of reducing elution of lead from a lead-containing copper alloy, characterized by the step of immersing the lead-containing copper alloy in an alkaline etching solu- 45

tion to which an oxidant has been added to remove lead on the surface thereof.

2. (Amended) A processing method of reducing elution of lead from a lead-containing copper alloy according to claim 1, wherein either one of an oxidant or a chelating agent, or both, are added to the alkaline etching solution.

3. (Amended) A processing method of reducing elution of lead from a lead-containing copper alloy, characterized by the step of immersing the lead-containing copper alloy in chromic acid solution to which fluoride has been added to remove lead on the surface thereof.

4. (Deleted)

5. (Amended) A processing method of reducing elution of lead from a lead-containing copper alloy, characterized by the step of immersing the lead-containing copper alloy in a chromate solution to which phosphoric acid has been added to form a chromate film on the surface thereof.

6. (Deleted)

7. (Amended) A processing method of reducing elution of lead from a lead-containing copper alloy, characterized by the step of immersing the lead-containing copper alloy in an alkaline etching solution to remove lead on the surface thereof, and subsequently immersing the same in a chromic solution to which fluoride has been added to remove lead on the surface thereof.

8. (Amended) A processing method of reducing elution of lead from a lead-containing copper alloy, characterized by the step of immersing the lead-containing copper alloy in an alkaline etching solution to which an oxidant has been added to remove lead on the surface thereof, and subsequently immersing the same in a chromate solution to form a chromate film on the surface thereof.

9. (Amended) A processing method of reducing elution of lead from a lead-containing copper alloy, characterized by the step of immersing the lead-containing copper alloy in chromic acid to which fluoride has been added to remove lead on the surface, and subsequently immersing the same in a chromate solution to form a chromate film on the surface thereof.

10. (Amended) A processing method of reducing elution of lead from a lead-containing copper alloy, characterized by the step of immersing the lead-containing copper alloy in an alkaline solution to 50

selectively remove lead on the surface thereof, and then immersing the same in chromic acid solution to remove further lead on the surface thereof, and subsequently immersing the same in a chromate solution to which phosphoric acid has been added to form a chromate film on the surface thereof.

11. (Deleted)

12. (Amended) A drinking water service fitting made of a lead-containing copper alloy, characterized by the step of immersing a lead-containing copper alloy material in an alkaline etching solution to which an oxidant has been added to remove lead on the surface thereof.

13. (Amended) A drinking water service fitting made of a lead-containing copper alloy, characterized by the step of immersing a lead-containing copper alloy material in a chromic acid solution to which fluoride has been added to remove lead on the surface thereof.

14. (Amended) A drinking water service fitting made of a lead-containing copper alloy, characterized by the step of immersing a lead-containing copper alloy material in a chromate solution to which phosphoric acid has been added to form a chromate film on the surface thereof.

15. (Amended) A drinking water service fitting made of a lead-containing copper alloy, characterized by the step of immersing a lead-containing copper alloy material in an alkaline etching solution to which an oxidant has been added to remove lead on the surface thereof, and subsequently immersing the same in a chromate solution to form a chromate film on the surface thereof.

16. (Amended) A drinking water service fitting made of a lead-containing copper alloy, characterized by the step of immersing a lead-containing copper alloy material in an alkaline etching solution to remove lead on the surface thereof, and subsequently immersing the same in a chromic acid solution to which fluoride has been added to remove lead on the surface thereof.

17. (Amended) A drinking water service fitting made of a lead-containing copper alloy, characterized by the step of immersing a lead-containing copper alloy material in a chromic acid solution to which fluoride has been added to remove lead on the surface thereof, and subsequently immersing the same in a chromate solution to form a chromate film on the surface thereof.

18. (Amended) A drinking water service fitting made of

a lead-containing copper alloy, characterized by the step of immersing a lead-containing copper alloy material in an alkaline solution to remove lead on the surface thereof, and then immersing the same in a chromic acid solution to remove lead on the surface thereof, and subsequently immersing the same in a chromate solution to which phosphoric acid has been added to form a chromate film on the surface thereof.

19. (Added) A plating method of reducing elution of lead from a lead-containing copper alloy for plating the outer surface of the lead-containing copper alloy and at the same time, removing lead on the inner surface thereof.

20. (Added) A plating method of reducing elution of lead from a lead-containing copper alloy according to claim 19, wherein chromium plating is effected after nickel plating.

21. (Added) A plating method of reducing elution of lead from a lead-containing copper alloy according to claims 19 and 20, wherein an oxidant is contained in an alkaline degreasing solution for a cleaning step before plating.

22. (Added) A plating method of reducing elution of lead from a lead-containing copper alloy according to claim 20, wherein fluoride is contained in a plating solution for chromium plating.

23. (Added) A plating method of reducing elution of lead from a lead-containing copper alloy according to claims 19 and 20, wherein the lead-containing copper alloy is immersed in a chromate solution after plating the outer surface thereof to form a chromate film on the inner surface thereof.

24. (Added) A plating method of reducing elution of lead from a lead-containing copper alloy according to claims 19 and 20, wherein the lead-containing copper alloy is immersed in an alkaline degreasing solution for a cleaning step before plating in which an oxidant is contained, and plating is effected, after nickel plating, in a chromium plating solution in which fluoride is contained.

25. (Added) A drinking water service fitting made of a lead-containing copper alloy, characterized by the step of plating the outer surface of the lead-containing copper alloy and at the same time, removing lead on the inner surface thereof.

26. (Added) A drinking water service fitting made of a lead-containing copper alloy according to claim 25, wherein chromium plating is effected after nickel plating.

27. (Added) A drinking water service fitting made of a lead-containing copper alloy according to claims 25 and 26, wherein an oxidant is contained in an alkaline degreasing solution for a cleaning step before plating. 5
28. (Added) A drinking water service fitting made of a lead-containing copper alloy according to claim 26, wherein fluoride is contained in a plating solution for chromium plating. 10
29. (Added) A drinking water service fitting made of a lead-containing copper alloy according to claims 25 and 26, wherein the lead-containing copper alloy is immersed in a chromate solution after plating the outer surface thereof, to form a chromate film on the inner surface thereof. 15
30. (Added) A drinking water service fitting made of a lead-containing copper alloy according to claims 25 and 26, wherein the lead-containing copper alloy is immersed in an alkaline degreasing solution for a cleaning step before plating in which an oxidant is contained, and chromium plating is effected, after nickel plating, in a chromium plating solution in which fluoride is contained. 20 25
31. (Added) A plating method of reducing elution of lead from a lead-containing copper alloy according to claims 19 and 20, wherein the lead-containing copper alloy is immersed in an alkaline degreasing solution for a cleaning step before plating in which an oxidant is contained, and plating is effected, after nickel plating, in a chromium plating solution in which fluoride is contained, and the lead-containing copper alloy is subsequently immersed in a chromate solution to form a chromate film on the inner surface thereof. 30 35
32. (Added) A drinking water service fitting made of a lead-containing copper alloy according to claims 25 and 26, wherein the lead-containing copper alloy is immersed in an alkaline degreasing solution for a cleaning step before plating in which an oxidant is contained, and plating is effected, after nickel plating, in a chromium plating solution in which fluoride is contained, and the lead-containing copper alloy is subsequently immersed in a chromate solution to form a chromate film on the inner surface thereof. 40 45 50
33. (Added) A plating method of reducing elution of lead according to claims 19 and 20, wherein phosphoric acid is contained in a chromate solution. 55
34. (Added) A plating method of reducing elution of lead according to claims 25 and 26, wherein phosphoric acid is contained in a chromate solution, and a drinking water service fitting made of a lead-containing copper alloy available from the plating method.

FIG. 1

Composition of alkaline solution for immersion				Lead concentration (ppb)	
Main components	Oxidant	Chelating agent	Surface active agent	Alkaline immersion only	Immersion in chromic acid after immersion in alkaline solution
Untreated sample	—	—	—	600	
Sodium orthosilicic acid 50g/l (pH about 13)	—	—	—	90	50
Sodium hydroxide 50g/l (pH about 14)	—	—	—	80	30
Sodium hydroxide 50g/l	Meta-nitrobenzene sodium sulfonate Sodium 10g/l	—	—	61	17
Sodium hydroxide 50g/l	Sodium hypochlorite 30mg/l	—	—	68	19
Sodium hydroxide 50g/l	Meta-nitrobenzene sodium sulfonate Sodium 2g/l	EDTA 2g/l Ethylene diamine 2g/l	—	53	12

FIG. 2

Type of chromium plating solution	Lead concentration (ppb)
Immersion in alkaline solution only (No immersion in chromium plating solution)	63
Sargent chromium plating bath consisting of chromic anhydride (200g/l) and sulfuric acid (2g/l)	18
Chromium fluoride plating bath on the market (F content of about 1g/l)	12

FIG. 3

No.	Composition of chromate solution				Lead concentration (ppb)
	Chromic anhydride	85% phosphoric acid	96% sulfuric acid	50% sulfuric acid	
1	15 g/l	10 ml/l	5 ml/l	5 ml/l	2
2	15 g/l	10 ml/l	5 ml/l	—	2
3	15 g/l	—	5 ml/l	5 ml/l	9
4	—	10 ml/l	5 ml/l	5 ml/l	10
5	No chromate step available (Immersion in chromium acid only after immersion in alkaline etching solution)				12

FIG. 4

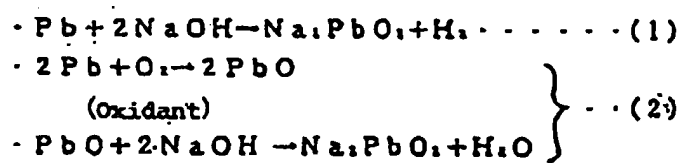
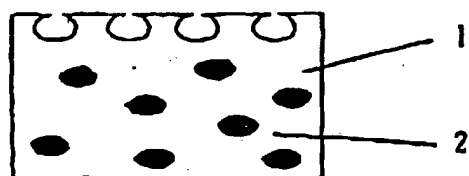


FIG. 5

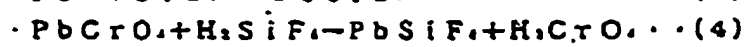
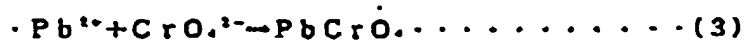
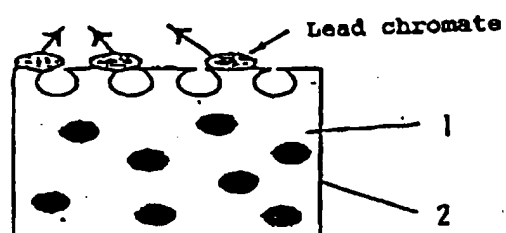


FIG. 6

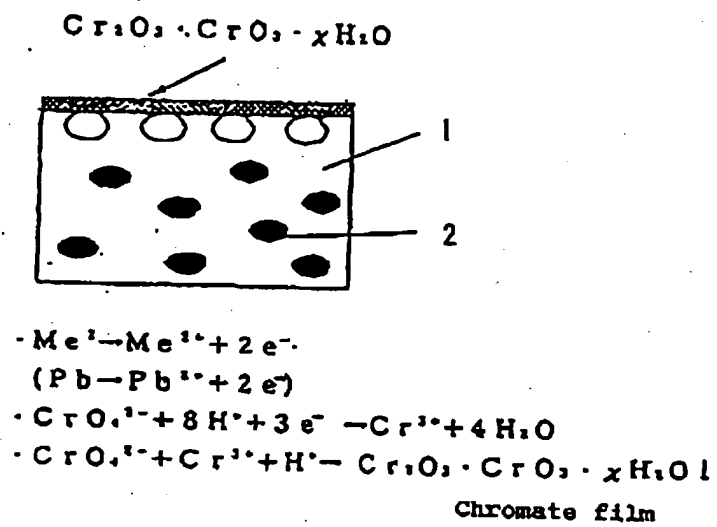
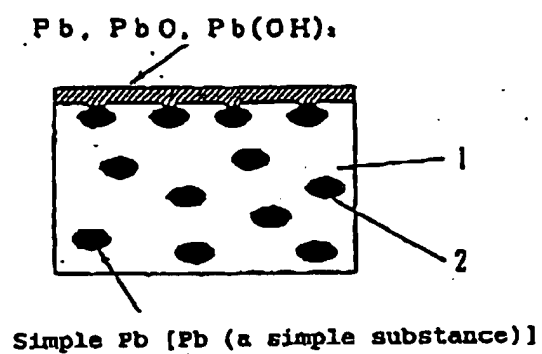


FIG. 7



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP98/05429

A. CLASSIFICATION OF SUBJECT MATTER		
Int.Cl. ⁶ C23F1/34, 1/44, C23C22/24		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
Int.Cl. ⁶ C23F1/32-1/44, C23C22/24-22/33		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-1998 Kokai Jitsuyo Shinan Koho 1971-1998 Jitsuyo Shinan Toroku Koho 1996-1998		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
PK	JP, 10-72683, A (TOTO Ltd.), 17 March, 1998 (17. 03. 98), Claims (Family: none)	1-2, 12
A	JP, 50-148253, A (Hodogaya Chemical Co., Ltd.), 27 November, 1975 (27. 11. 75), Claims (Family: none)	1-18
A	JP, 53-52252, A (Nippon Soda Co., Ltd.), 12 May, 1978 (12. 05. 78), Claims (Family: none)	1-18
A	JP, 64-8278, A (Mitsui Mining & Smelting Co., Ltd.), 12 January, 1989 (12. 01. 89), Claims (Family: none)	1-18
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "I" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 4 February, 1999 (04. 02. 99)		Date of mailing of the international search report 16 February, 1999 (16. 02. 99)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)